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## EVALUATION OF CRYSTALLIZATION CAPACITY OF GLASSES

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A temperature-concentration dependence of the linear velocity of crystal growth (LVCG) of diopside for potassium-bearing glasses of the system  $\text{CaO} - \text{MgO}(\text{Al}_2\text{O}_3) - \text{SiO}_2$  is determined based on adaptation of the Turnbull-Cohen theoretical equation, and a relationship between the LVCG of devitrite and cristobalite and the chemical composition of glasses located in the respective areas on the phase diagram of the  $\text{Na}_2\text{O} - \text{CaO} - \text{SiO}_2$  system phase diagram is established.

Crystallization capacity is one of the most essential technological properties in the production of various materials: glasses, glass ceramics, portland cement, etc. Crystallization capacity in glasses is undesirable, whereas in producing glass ceramics with finely disperse volume crystallization, which imparts enhanced mechanical and physicochemical properties, good crystallization capacity is an obligatory condition.

Linear velocity of crystal growth (LVCG) is one of the characteristics of crystallization capacity in glasses and glass-forming melts. Experimental methods for estimating crystallization capacity are labor-consuming. Although there are numerous methods for calculation of various properties of glasses and glass-forming melts based on their chemical compositions, there is as yet no method for calculation of LVCG. The purpose of our study was to develop a method for calculation of LVCG based on the chemical compositions of glasses in the framework of certain fundamental systems, which serve as a basis for the production of glass articles and glass ceramics.

An equation used to describe the temperature dependence of LVCG was the Turnbull–Cohen equation derived to determine the velocity of crystallization of supercooled liquids (and the rate of crystal dissolution above the liquidus temperature), including glasses [1]:

$$U = \frac{\phi RT}{3\pi a_0^2 N_A \eta} \left[ 1 - \exp\left(\frac{-\Delta H_f \Delta T}{RTT_m}\right) \right], \quad (1)$$

where  $\phi$  is a coefficient expressing the share of areas on the crystal surface in which atoms (molecules) become bound;  $R$  is the universal gas constant;  $T$  is the temperature,  $a_0$  is the transition distance (the thickness of the phase boundary layer),  $N_A$  is the Avogadro number;  $\eta$  is the viscosity;  $\Delta H_f$  is

the melting heat of formed crystals;  $\Delta T = T_{\text{liq}} - T$  is the supercooling with respect to the liquidus temperature  $T_{\text{liq}}$ ;  $T_m$  is the melting temperature of formed crystals.

Analysis of the literature indicated that the use of this equation for describing crystal growth velocity yields a substantial divergence from the experimental data, which is accounted by, in particular, by the fact that it is not quite clear how to determine the parameters  $\phi$  and  $a_0$ . An assumption has been made that  $\phi$  depends on temperature, i.e., it increases with intensification of the process.

The above expression had to be adapted in order to use it for the approximation of experimental data on LVCG of real glasses using the function  $U = f(T)$  and for the calculation of LVCG based on the chemical composition of glasses.

The following empirical form of the dependence of the parameter  $\phi$  in Eq. (1) on supercooling is proposed:

$$\phi = K' \exp\left(w \frac{\Delta T}{T}\right), \quad (2)$$

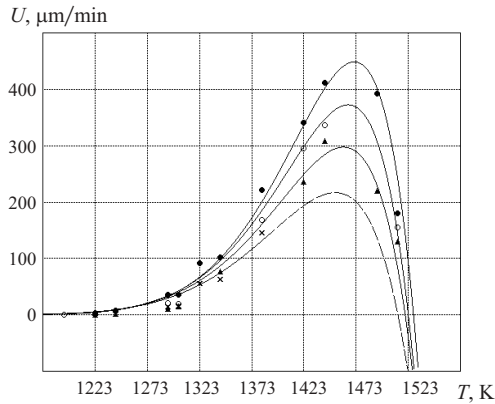
where  $0 < K' \leq 1$  and  $w \geq 0$  are constants for a particular glass composition.

The adapted Turnbull–Cohen equation is obtained from Eq. (1) by substituting expression (2) and combining all constants into a single constant:

$$U(T) = \frac{K \exp\left(w \frac{T_{\text{liq}} - T}{T}\right) T}{10^{\frac{A+B}{T-T_0}}} \times \left[ 1 - \exp\left(\frac{-x_x \Delta H_f (T_{\text{liq}} - T)}{RTT_m}\right) \right], \quad (3)$$

where  $K$  is the constant;  $x_x$  is the molar part of the compound formed in the initial glass.

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**Fig. 1.** LVCg of diopside in glasses: Dots) experimental data; ●) P1; ○) P2; ▲) P3; ×) P4; curves) approximation based on equation (3).

The temperature dependence of viscosity is described by the Fogel – Fulcher – Tamman equation (parameters  $A$ ,  $B$ , and  $T_0$ ). The effect of using the parameter  $x_x$  for nonstoichiometric compositions of glass-forming silicate melts is described in [2].

The function  $U = f(T)$  set by expression (3) was used to approximate the known experimental data on LVCg (up to 50 compositions). The viscosity was calculated based on chemical compositions of glasses using the known methods, the parameters  $K$  and  $w$  were calculated using experimental data ensuring the maximum accuracy of approximation,  $T_m$  and  $\Delta H_f$  are reference data, and  $T_{liq}$  was determined based on experimental LVCg curves and phase diagrams. It was found that the function  $U = f(T)$  adequately described the temperature dependences of LVCg.

The adapted Turnbull – Cohen equation was used to express LVCg as a function of the chemical composition of glasses. To determine LVCg based on the chemical composition of glasses using the adapted equation, it is necessary to calculate the glass viscosity and to establish the effect of their chemical composition on the parameters  $K$ ,  $w$ , and  $T_{liq}$  for the considered systems within certain limits of component concentrations.

We investigated potassium-bearing glasses of the system  $\text{CaO} - \text{MgO} - \text{SiO}_2$ , which is the fundamental system in the production of glass ceramics with a pyroxene crystalline phase. Pyroxene glasses with different molar parts of diopside  $x_{Di}$  were synthesized (Table 1) and  $\text{K}_2\text{O}$  was introduced to improve the technological properties of glasses. The compositions were selected in such a way that after the release of diopside from the initial glass P1 the chemical composition of the residual glass keeps changing in the direction of  $\text{P1} \rightarrow \text{P2} \rightarrow \text{P3} \rightarrow \text{P4}$ . Diopside was released in the crystallization of glasses P1 – P4.

Using the hardening method, the temperature dependence of the LVCg of diopside was determined for each composition. The obtained dependences were approximated by the function (3) (Fig. 1, Table 2). The liquidus temperature was determined from the experimental curves of LVCg.

**TABLE 1**

Glass	Mass content, %				Molar part of diopside
	$\text{K}_2\text{O}$	$\text{CaO}$	$\text{MgO}$	$\text{SiO}_2$	
P1	4.00	20.74	14.81	60.45	0.8273
P2	6.00	18.15	12.96	62.89	0.7365
P3	8.00	15.55	11.11	65.34	0.6424
P4	10.00	12.97	9.25	67.78	0.5450

**TABLE 2**

Parameter*	Glass			
	P1	P2	P3	P4
$T_{liq}$ , K	1528	1523	1520	1513
$x_{Di} \Delta H_f$ , ** kJ/mole	57.9	51.5	44.9	38.1
$A$	–3.336	–3.314	–3.278	–3.258
$B$	4306	4373	4465	4592
$T_0$ , K	688.7	673.2	654.6	632.0

\*  $T_m = 1664$  K,  $K \times 10^6 = 5.0$ ,  $w = 0$ .

\*\* According to various data, the melting heat of diopside varies from 68 to 96 kJ/mole; the value used in calculation was 70 kJ/mole.

It follows from data in Table 2 that the parameters  $K$  and  $w$  are constant for glasses P1 – P4, the parameter  $w$  characterizes an increasing LVCg in the left (ascending) branch of the curve  $U = f(T)$ ,  $T_{liq}$  in the specified range of compositions linearly depends on crystallization heat, and the function  $T_{liq} = f(x_x, \Delta H_f)$  is close to linear.

The principles of calculation of LVCg based on the chemical composition of potassium-bearing glasses of the  $\text{CaO} - \text{MgO} - \text{SiO}_2$  system located within the diopside range on the phase diagram is as follows:

- the parameters  $K$  and  $w$  are constant:  $K = 5 \times 10^{-6}$ ,  $w = 0$ ;
- the viscosity (parameters  $A$ ,  $B$ , and  $T_0$ ) are calculated based on the chemical composition using the known methods;
- $x_{Di}$  is determined based on the chemical composition of glass expressed in molar parts;
- $T_{liq}$  in accordance with experimental data is calculated from the formula  $T_{liq} = 51x_{Di} + 1486$ ;
- $\Delta H_f = 70 \times 10^3$  J/mole.

It is experimentally established that introduction of the Chermak aluminate radical  $\text{CaAl}_2\text{SiO}_6$  into glasses of the considered system while preserving a preset estimated diopside content decreases the liquidus temperature and the LVCg, which agrees with the known concepts of the physical chemistry of silicates regarding the crystallization processes:  $\text{Al}_2\text{O}_3$  increases viscosity by decreasing LVCg, and introduction of a new component, as a rule, decreases  $T_{liq}$ .

In addition to the pyroxene system  $\text{CaO} - \text{MgO} (\text{Al}_2\text{O}_3) - \text{SiO}_2$ , we processed experimental data found in the literature on crystallization of glasses of the  $\text{Na}_2\text{O} - \text{CaO} -$

TABLE 3

Glass	Mass content, %			Emerging phase	Molar part of emerging phase	Region in phase diagram
	Na <sub>2</sub> O	CaO	SiO <sub>2</sub>			
C1	18	16	66	Devitrite	0.57	Wollastonite
C2	16	16	68	The same	0.57	The same
C3	14	16	70	"	0.57	"
C4	12	16	72	"	0.57	"
C5	18	14	68	"	0.50	Devitrite
C6	16	14	70	"	0.50	The same
C7	14	14	72	"	0.50	"
C8	12	14	74	"	0.50	Tridimite
C9	18	12	70	"	0.43	Devitrite
C10	16	12	72	"	0.43	The same
C11	14	12	74	Cristobalite	0.74	Tridimite
C12	12	12	76	The same	0.76	The same
C13	18	10	72	Devitrite	0.36	Devitrite
C14	16	10	74	Cristobalite	0.73	Tridimite
C15	14	10	76	The same	0.76	The same
C16	12	10	78	"	0.78	"

SiO<sub>2</sub> system, which is the basic system in the production of glass articles (Table 3). Similarly to pyroxene glasses, it was possible to establish a relationship between the LVCG of emerging crystalline phases and the chemical composition of glass (Table 4, Fig. 2). The liquidus temperature was determined based on the phase diagram of the Na<sub>2</sub>O – CaO – SiO<sub>2</sub> system using experimental LVCG curves. The compositions C1 – C4 in the phase diagram are located within the wollastonite range near the incongruent point; therefore, after primary crystallization of wollastonite, devitrite Na<sub>2</sub>O · 3CaO · 6SiO<sub>2</sub> is formed in them.

As the devitrite concentration in glass decreases,  $T_{\text{liq}}$  and LVCG at the given temperatures decrease as well, which cor-

responds to a deviation of the composition from the devitrite stoichiometry and agrees with the known concepts. For compositions in which the devitrite content is constant, the LVCG decreases with decreasing Na<sub>2</sub>O content in glass, which is due to increased viscosity. The dependence of LVCG on the chemical composition of glass is determined by the parameters  $A$ ,  $B$ ,  $T_0$ ,  $x_x$ , and  $T_{\text{liq}}$ , and for glasses crystallized with formation of cristobalite is mainly determined by the parameter  $T_{\text{liq}}$ .

Initial data for the calculation of LVCG of devitrite and cristobalite based on the chemical composition of glasses are taken from the phase diagram of the Na<sub>2</sub>O – CaO – SiO<sub>2</sub> system depending on the location of figurative points of these compositions:

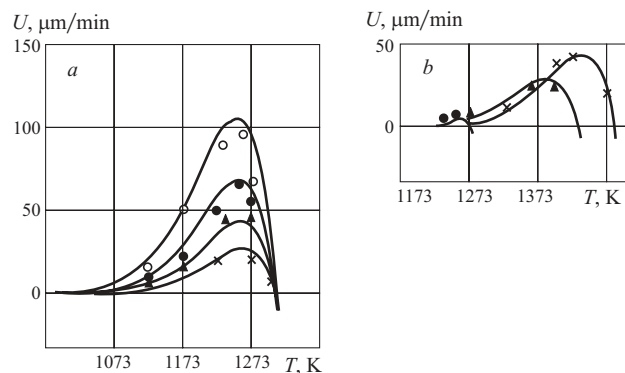
- parameters  $K$  and  $w$  are constant:  $K = 7.5 \times 10^{-6}$  for the devitrite range and  $K = 3.5 \times 10^{-6}$  for the cristobalite range;
- $w = 1$ ;
- viscosity (parameters  $A$ ,  $B$ ,  $T_0$ ) is calculated based on the chemical composition using the known methods;
- $x_x$  is determined from the chemical composition of glass;
- $T_{\text{liq}}$  is revealed from the phase diagram;
- the melting heat of devitrite is  $60 \times 10^3$  J/mole and that of cristobalite is  $8.8 \times 10^3$  J/mole.

The established temperature-concentration dependences of LVCG of solid phases in the system can serve as a basis for the evaluation of the crystallization capacity of industrial container and sheet glasses, since in reducing compositions to the Na<sub>2</sub>O – CaO – SiO<sub>2</sub> system, they fall within the considered range. However, it is necessary to take into account

TABLE 4

Glass	Phase	Parameters of Eq. (3)*						
		$T_{\text{liq}}$ , K	$T_m$ , K	$K \times 10^6$	$x_x, \Delta H_f$ , kJ/mole	$A$	$B$	$T_0$ , K
C1	Devitrite	1333	1573	7.5	34.2	– 2.916	4190	513.1
C2	The same	1333	1573	7.5	34.2	– 2.893	4068	552.3
C3	"	1333	1573	7.5	34.2	– 2.872	3949	591.3
C4	"	1333	1573	7.5	34.2	– 2.859	3836	629.8
C5	"	1316	1573	7.5	29.9	– 3.040	4173	537.8
C6	"	1313	1573	7.5	29.9	– 3.134	4295	551.0
C7	"	1308	1573	7.5	29.9	– 3.229	4419	564.0
C8	"	1308	1573	7.5	29.9	– 3.318	4535	577.4
C9	"	1283	1573	7.5	25.8	– 3.161	4151	563.3
C10	"	1283	1573	7.5	25.8	– 3.373	4518	550.2
C11	Cristobalite	1373	1986	3.5	6.5	– 3.583	4885	536.9
C12	The same	1453	1986	3.5	6.7	– 3.796	5253	523.5
C13	Devitrite	1253	1573	7.5	21.6	– 3.279	4121	589.6
C14	Cristobalite	1273	1986	3.5	6.4	– 3.609	4735	549.0
C15	The same	1433	1986	3.5	6.7	– 3.937	5347	510.3
C16	"	1483	1986	3.5	6.9	– 4.266	5959	470.6

\*  $w = 1$ .



**Fig. 2.** LVCG of solid phases in glasses of system  $\text{Na}_2\text{O} - \text{CaO} - \text{SiO}_2$ : a) devitrite: ○) C5, ●) C6, ▲) C7, ×) C8; b) cristobalite: ●) C14, ▲) C15, ×) C16; curves) approximation based on equation (3).

the effect of additional oxides on LVCG. The crystallization capacity of industrial glasses was investigated in [3 – 6]. It is known that cristobalite is the first compound formed in industrial glasses of the  $\text{Na}_2\text{O} - \text{CaO} - \text{SiO}_2$  system with slight additives of  $\text{Al}_2\text{O}_3$  (up to 2.5 wt.%) and  $\text{MgO}$  (up to 2.0%). Accordingly, the temperature dependence of LVCG of cristobalite determines the technological characteristics related to a risk of glass crystallization: upper crystallization limit, temperature, LVCG maximum, etc.

The obtained temperature-concentration dependences of cristobalite in glasses of the  $\text{Na}_2\text{O} - \text{CaO} - \text{SiO}_2$  system

served as a basis for the calculation of technological characteristics of industrial container and sheet glasses of the system  $\text{Na}_2\text{O} - \text{CaO} - \text{MgO}$  (up to 2.0 wt.%  $\text{Al}_2\text{O}_3$  and up to 2.5 wt.%  $\text{SiO}_2$ ). The additional oxides modify the content of compounds emerging in crystallization, the liquidus temperature, and the viscosity. On the whole the obtained temperature dependence of LVCG of industrial glasses and calculated technological characteristics related to the risk of their crystallization agree with the literary data and can be used in the synthesis of industrial glass compositions.

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